

Unaxisymmetric Non-Fused Electron Acceptors for Efficient Polymer Solar Cells

Si-Ya Liu^{a,†}, Di Wang^{a,†}, Tian-Jiao Wen^a, Guan-Qing Zhou^b, Hai-Ming Zhu^b, Hong-Zheng Chen^a, and Chang-Zhi Li^{a*}

^a State Key Laboratory of Silicon Materials, MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

^b Department of Chemistry, Zhejiang University, Hangzhou 310027, China

Electronic Supplementary Information

Abstract To develop photovoltaics embracing the both features of high performance and low cost has drawn attentions of researchers, yet representing the significant challenges. In this work, two non-fused ring acceptors (NFRAs), namely p-PTIC4Cl and t-PTIC4Cl, were developed via a short synthetic route. By tethering unaxisymmetric aromatic chains to thienyl bridge of NFRAs, we revealed that the tuning of aromatic chains allows modulating the self-assembly and stacking of NFRAs in solid, hence influencing their optoelectronic and photovoltaic properties. As results, p-PTIC4Cl, consisting of 3-hexylbenzene with large axial angle to backbone, can achieve superior PCE of 11.30% than that of t-PTIC4Cl with 2-hexylthiophene chains (PCE of 6.49%), when pairing with polymer donor PBDB-TF. Despite of the only subtle structural difference, the p-PTIC4Cl based blend films possess better exciton dissociation and charge transfer rates, as well as photostability, to those of t-PTIC4Cl based blends.

Keywords Polymer solar cells; Non-fused ring acceptor; Unaxisymmetric aromatic chains; Photostability

Citation: Liu, S. Y.; Wang, D.; Wen, T. J.; Zhou, G. Q.; Zhu, H. M.; Chen, H. Z.; Li, C. Z. Unaxisymmetric non-fused electron acceptors for efficient polymer solar cells. *Chinese J. Polym. Sci.* 2022, 40, 944–950.

INTRODUCTION

Single-junction polymer solar cells (PSCs) have recently achieved over 18% power conversion efficiencies (PCEs).^[1–6] With these encouraging progresses being made,^[7–14] to embed photovoltaic materials with desirable performance-cost balance becomes essential for further advancing PSCs toward practical relevance. In this regards, the design of non-fused ring acceptors (NFRAs),^[15,16] wherein non-covalent interaction is employed to reinforce the planarity and rigidity of conjugated backbones,^[17] has drawn attentions of researchers,^[18] owing to the reduced synthetic complexity of molecules by avoiding multi-step ring-fusing reaction among aromatic units, such as cyclopentadithiophene (CPDT),^[19–22] thiophene,^[23–27] bithiophene^[28] and phenyl group.^[29] We have previously shown that the fully non-fused ring acceptors, with alkoxy-phenyl core and thienyl bridge, can be made through two-step synthesis, meanwhile delivering decent photovoltaic performance in PSCs.^[16,17,29,30] Impressively, the recent development of NFRAs

with terthiophene and bithiophene skeleton has enabled the derived PSCs with excellent PCEs over 15%.^[31,32] These efforts clearly illustrate the promising perspectives in designing new photovoltaic materials with the fine balance between performance and production cost. Therefore, to advance this line of research becomes meaningful, which requires to deepen the structure-property understandings of NFRAs. Besides of the structural tuning of non-fused backbones, we have proposed that the aromatic chains play roles on regulating the solid stacking and optoelectronic properties of NFRAs.^[30] Meanwhile, It is also shown that the unaxisymmetric aromatic chains play roles on optimizing the photovoltaic properties of fused ring electron acceptors.^[33–35] These strategies can potentially provide new structural taps to optimize the photovoltaic performance of NFRAs, yet to be further explored.

Herein, two fully non-fused ring acceptors, namely p-PTIC4Cl and t-PTIC4Cl, have been developed by tethering thienyl bridge with unaxisymmetric aromatic chains, 3-hexylbenzene and 2-hexylthiophene, respectively. It is revealed that the tuning of unaxisymmetric aromatic chains could effectively modulate the self-assembly and stacking of NFRAs in solid, hence influencing their optoelectronic and photovoltaic properties. As results, p-PTIC4Cl, consisting of 3-hexylbenzene with large axial angle to backbone, can achieve superior PCE of 11.30% than that of t-PTIC4Cl with 2-hexylthiophene at

* Corresponding author, E-mail: czli@zju.edu.cn

† These authors contributed equally to this work.

Special Issue: Organic Photovoltaic Polymers

Received March 7, 2022; Accepted April 2, 2022; Published online June 21, 2022

small axial angle (PCE of 6.49%), when pairing with polymer donor PBDB-TF. The p-PTIC4Cl based blend films were also found to possess better exciton dissociation and charge transfer rates, as well as photostability, than the t-PTIC4Cl based blends. Overall, this work provides the valuable structure-property understandings to optimize the optoelectronic properties of cost-effective electron acceptors.

EXPERIMENTAL

Please see the electronic supplementary information (ESI) for the description of materials and experiments.

RESULTS AND DISCUSSION

The chemical structures of p-PTIC4Cl and t-PTIC4Cl are shown in

Fig. 1(a), and their synthetic routes are described in ESI. Thienyl bridges with two kinds of unaxisymmetrical side chains, 3-(3-hexylphenyl) thiophene and 5-hexyl-2,3'-bithiophene were synthesized by Suzuki coupling reaction, then derivatized into aldehydes through Vilsmeier-Haack reaction. The non-fused ring backbones consisting of alkoxy-phenyl core and thienyl bridge were synthesized through C-H activation coupling, then followed by Knoevenagel condensation with 2-(5,6-dichloro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (IC-2Cl) terminal groups to yield target molecules, p-PTIC4Cl and t-PTIC4Cl, respectively. Molecular structures were confirmed by proton and carbon nuclear magnetic resonance (^1H - and ^{13}C -NMR), matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectroscopy. Their thermal properties (Fig. S1 in ESI) were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC),^[36] showing a

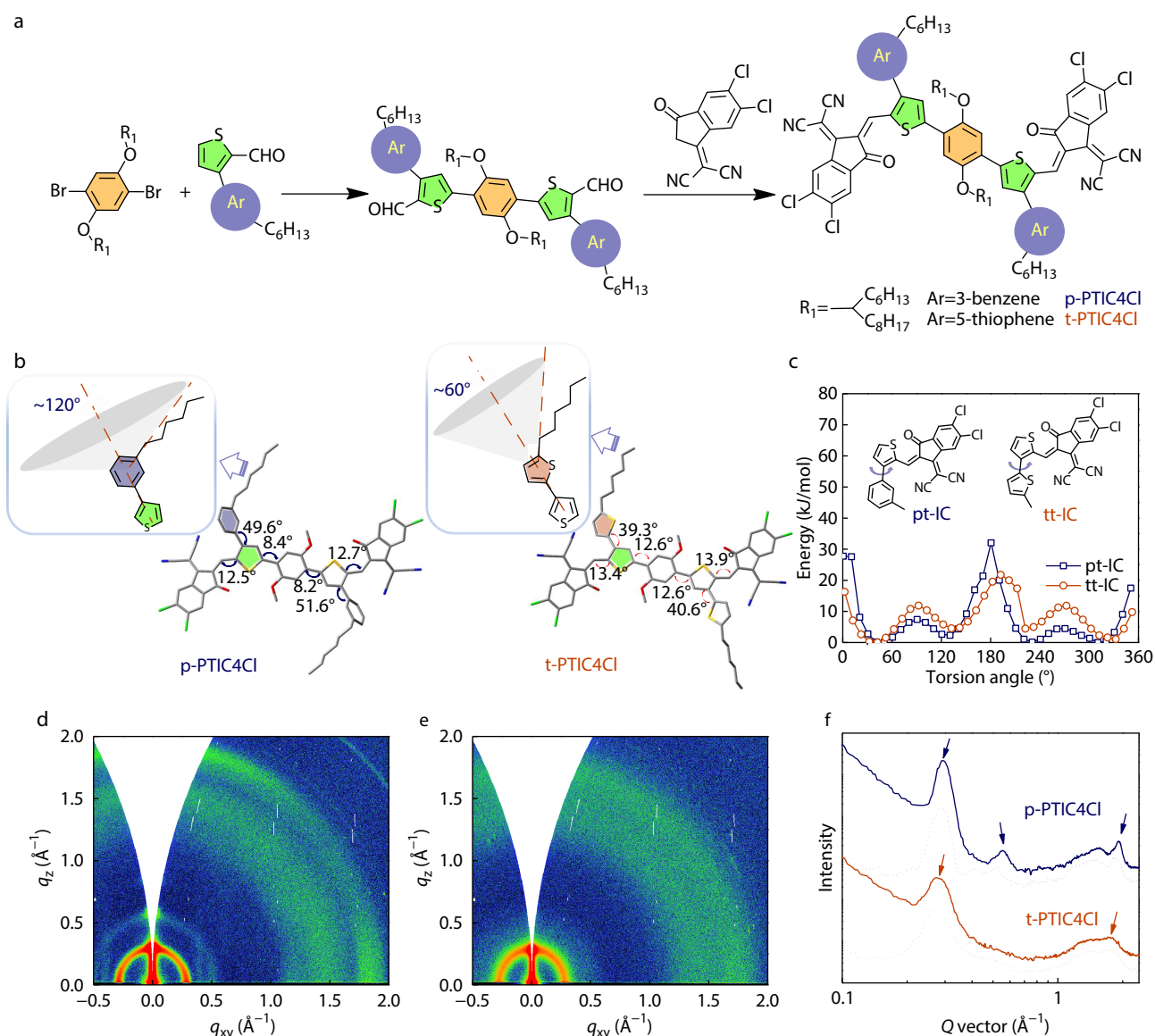


Fig. 1 (a) Synthetic route and (b) the optimized molecular geometries of NFRAs with the schematic diagram of unaxisymmetric aromatic chains, 3-hexylbenzene and 2-hexylthiophene, respectively. (c) Energy surface scan of model rotamers. The 2D-GIWAXS patterns of (d) p-PTIC4Cl and (e) t-PTIC4Cl neat films and (f) the corresponding line-cut profiles (solid line: out-of-plane, dashed line: in-plane).

melting peak at 221 °C and a crystallization peak at 193 °C for p-PTIC4Cl, whereas no phase transition peak can be found for t-PTIC4Cl. It indicates that p-PTIC4Cl has better crystallinity than t-PTIC4Cl, with the subtle difference in aromatic side chains.

Density functional theory (DFT) calculation (Fig. S2, in ESI) illustrates the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of two NFRA at similar levels, to be $-3.51/-5.74$ eV (p-PTIC4Cl) and $-3.49/-5.71$ eV (t-PTIC4Cl), respectively. Both NFRA show planar backbones with relatively small dihedral angles among aromatic units, with the assistance of intramolecular noncovalent interactions^[17,30] (Fig. 1b). As shown in the optimized molecular geometries, 3-hexylbenzene unit, as six-member ring with axis angle of $\sim 120^\circ$, exhibits a large torsion angle ($\sim 50^\circ$) and high rotation barrier (~ 30 kJ/mol, calculated from model rotamer pt-IC) to the backbone skeleton (Fig. 1c). However, 2-hexylthiophene, five-member ring with axis angle of $\sim 60^\circ$, displays a small torsion angle ($\sim 40^\circ$) and low rotation barrier (~ 20 kJ/mol from model rotamer tt-IC). It indicates that the 2-hexylthiophene would be more conducive to the axis rotation (or vibration) in molecule, than that of 3-hexylbenzene. The rotation of alkyl chains along the axial angle would produce the spatial disturbance on the molecular interaction, hence influencing the molecular stacking and crystallinity of molecules in solid.

To investigate the effect of unaxisymmetric chains on molecular ordering of NFRA in solid, we first performed grazing incidence wide-angle X-ray scattering (GIWAXS) measurements of the as-cast neat films (Figs. 1d–1f). Both p-PTIC4Cl and t-PTIC4Cl films present the mixed face-on and edge-on orientation relative to the substrate, while p-PTIC4Cl films clearly exhibiting stronger diffraction peak intensities, thus better crystallinities than that of t-PTIC4Cl. The diffraction peaks located at $q_z=0.293$ Å⁻¹ ($d=21.44$ Å) for p-PTIC4Cl and $q_z=0.277$ Å⁻¹ ($d=22.68$ Å) for t-PTIC4Cl are indexed as (100) peaks, corresponding to the OOP lamellar stacking of NFRA. In addition, the π - π stacking in OOP direction could be indexed as (010) peak at $q_z=1.92$ Å⁻¹ ($d=3.27$ Å) for p-PTIC4Cl and $q_z=1.77$ Å⁻¹ ($d=3.54$ Å) for t-PTIC4Cl. It indicates that p-PTIC4Cl adapts tighter molecular stacking than t-PTIC4Cl in films. Interestingly, one additional diffraction peak at $q_z=0.56$ Å⁻¹ ($d=11.2$ Å) is found in p-PTIC4Cl film, while being absence in t-PTIC4Cl film, which is attributed to the long-range ordering of molecules along the backbone direction from end group stacking.^[37] It is a characteristic of molecule ordering of non-fullerene acceptors in solid that facilitates charge transport.

The optical properties of NFRA were characterized by Ultraviolet-visible (UV-Vis) absorption spectroscopy (Fig. 2a and Fig. S3 in ESI). The absorption peaks for solutions and as-cast films are recorded in Table 1. It shows that the annealed films

Table 1 Optoelectronic properties of p-PTIC4Cl and t-PTIC4Cl.

Materials	$\lambda_{\max}$ (nm)		λ_{onset} (nm)	E_g^{opt} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)
	solution	film				
p-PTIC4Cl	658	699	814	1.52	-5.81	-3.68
t-PTIC4Cl	663	716	798	1.55	-5.79	-3.62

possess the further bathochromic-shift of absorption peaks (to 756 nm of p-PTIC4Cl and 753 nm of t-PTIC4Cl), wherein t-PTIC4Cl presents the strong tendency of over aggregation (Fig. S3 in ESI). The optical bandgaps were calculated to be 1.52 eV for p-PTIC4Cl and 1.55 eV for t-PTIC4Cl. Cyclic voltammetry (CV) measurements were used to evaluate the LUMOs and the HOMOs of NFRA, to be -3.68 and -5.81 eV for p-PTIC4Cl and -3.62 and -5.79 eV for t-PTIC4Cl (Fig. 2b and Table 1).

To evaluate their photovoltaic properties, a medium bandgap polymer, PBDB-TF (PM6) as an electron donor was selected to pair with p-PTIC4Cl and t-PTIC4Cl (Fig. 2c). The absorption profiles (Figs. 2d and 2e) of the as cast blends display the strong absorption peak at 629 nm corresponding to PBDB-TF, while appearing with the relatively weak absorption peaks at 692 nm (p-PTIC4Cl) and 708 nm (t-PTIC4Cl). Note that thermal annealing (TA) treated blend films exhibit the significant bathochromic shift of absorption for NFRA with strong absorption peaks at 748 nm (p-PTIC4Cl) and 747 nm (t-PTIC4Cl), implying TA process enhances the aggregation of NFRA in blend films. What's more, the solvent additive (1-chloronaphthalene, CN) treatment further improves the intensity ratio for NFRA absorption peaks (relative to polymer absorption peaks), suggesting the NFRA aggregation was further enhanced. PSCs were fabricated with the conventional structure^[38] of ITO/PEDOT:PSS/PBDB-TF: NFRA/PFN-Br/Ag (Fig. 2f). The p-PTIC4Cl based PSCs by TA process exhibit the best PCE of 11.30%, with an open-circuit voltage (V_{oc}) of 0.90 V, a short-circuit current density (J_{sc}) of 18.01 mA·cm⁻² and a fill factor (FF) of 69.74% (Table 2). The photovoltaic parameters of PSCs from different processing conditions are displayed in Figs. 2(g) and 2(h) and Table S1 (in ESI). Note that the increase of J_{sc} and FF for the p-PTIC4Cl based PSCs by TA is probably due to the optimization of p-PTIC4Cl aggregation in BHJ blend. Whereas, the optimal device performance of t-PTIC4Cl based PSCs is obtained with the as cast blend films, achieving the PCE of 6.49% (with a V_{oc} of 0.94 V, a J_{sc} of 12.12 mA·cm⁻² and an FF of 57.39%). Both TA and CN treatments decrease device performance, especially on J_{sc} and FF, which is likely due to the tendency of over aggregation for t-PTIC4Cl in blend films. The external quantum efficiency (EQE) spectra reveal that p-PTIC4Cl PSCs exhibit higher EQE response than t-PTIC4Cl PSCs at the wide range of 350–850 nm (Fig. 2i, Figs. S2 and S3 in ESI). Meanwhile, the J_{sc} calculated by the integral of EQE spectra is 17.19 mA·cm⁻² and 11.49 mA·cm⁻² for p-

Table 2 Photovoltaic parameters of PBDB-TF: NFRA under AM 1.5G illumination (100 mW·cm⁻²).

NFRA	V_{oc} (V)	J_{sc} (mA·cm ⁻²)	FF (%)	PCE ^a (%)	J_{cal} ^b (mA·cm ⁻²)
p-PTIC4Cl	0.90 (0.89±0.01)	18.01 (17.88±0.13)	69.74 (69.42±0.32)	11.30 (11.16±0.14)	17.19
t-PTIC4Cl	0.94 (0.93±0.01)	12.12 (12.11±0.01)	57.39 (56.82±0.57)	6.49 (6.49±0.07)	11.49

^a Average values with standard deviations from 10 cells; ^b Calculated from the EQE spectra.

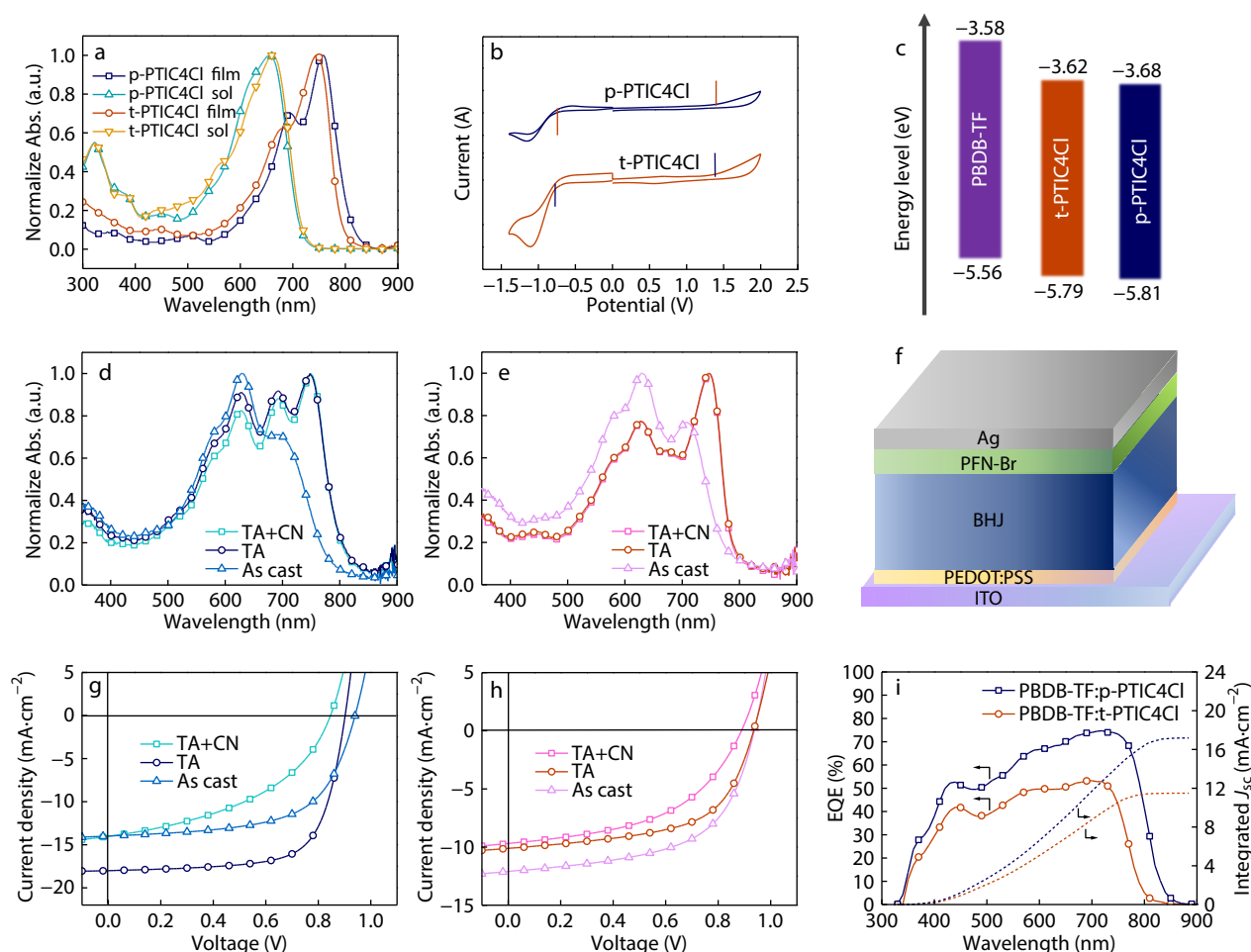


Fig. 2 (a) Normalized UV-Vis absorption spectra of NFRA films and solutions; (b) Cyclic voltammograms and (c) energy-level diagram of NFRA and PBDB-TF. Normalized UV-Vis absorption spectra of (d) PBDB-TF:p-PTIC4Cl and (e) PBDB-TF:t-PTIC4Cl blend films; (f) OSC structure and J - V curves of (g) PBDB-TF:p-PTIC4Cl and (h) PBDB-TF:t-PTIC4Cl devices under different processing conditions; (i) EQE spectra.

PTIC4Cl and t-PTIC4Cl devices, respectively, in consistent with the values obtained from the J - V curves (Table 2).

Further, the charge exciton dissociation probability $P(E, T)$, through the curves of photocurrent density (J_{ph}) versus the effective voltage (V_{eff}), is calculated to be 0.99 of p-PTIC4Cl devices and 0.91 of t-PTIC4Cl devices (Fig. 3a and ESI), indicating the better exciton dissociation and charge collection of p-PTIC4Cl devices than those of t-PTIC4Cl devices. In order to gain information on charge recombination of PSCs, their J - V curves of devices were measured and recorded under the various light intensities (Fig. 3b). The α value is calculated to be 0.997 for PBDB-TF:p-PTIC4Cl blends and 0.971 for PBDB-TF:t-PTIC4Cl blends, as $J_{sc} \propto (P_{light})^\alpha$, suggesting the suppressed bimolecular recombination of p-PTIC4Cl devices. The slopes of V_{oc} versus $\log P_{light}$ are calculated to be 1.043 and 1.104 kT/q for p-PTIC4Cl and t-PTIC4Cl PSCs (in ESI), respectively, implying the mitigated monomolecular recombination in p-PTIC4Cl based devices. Overall, the results suggest the suppressed charge recombination of p-PTIC4Cl devices, which is consistent with the higher J_{sc} and FF values. The photoluminescence (PL) spectra of neat NFRA and blend films are displayed in Fig. 3(c), wherein the PL quenching efficiencies are detected to be 92.32% for p-PTIC4Cl blend and

79.17% for t-PTIC4Cl blend. Time-resolved photoluminescence spectroscopy (TRPL) (Fig. S4 in ESI) also revealed that the faster PL decay of p-PTIC4Cl blends (89.65 ps) over that of t-PTIC4Cl blend films (95.62 ps). These results clearly indicate that there present more efficient charge and energy transfer in PBDB-TF:p-PTIC4Cl blend films, than those of PBDB-TF:t-PTIC4Cl.

Femtosecond transient absorption (fs-TA) spectroscopy were further measured to evaluate the exciton and hole transfer processes^[39,40] of neat and blend films. For TA spectra, we used 750 nm pump pulse to selectively excited NFRA and then measured the relative transmittance change ($\Delta T/T$) by a white light continuum. The 2D color plot of fs-TA spectra and curves of representative delay times are shown in Figs. 3(d) and 3(e) and Fig. S5 (in ESI). Note that PBDB-TF:NFRA blend films show new bleach peaks at ~ 570 nm and ~ 620 nm, corresponding to the ground state bleach (GSB) of PBDB-TF, from which the information related to the photoinduced hole transfer from NFRA to PBDB-TF can be extracted. As shown in Fig. 3(f), we chose the signals at 595 nm to represent the hole transfer kinetics of blend films where there is no signal for the photoexcited NFRA. The kinetic curves (Table S3 in ESI) were obtained with the biexponential fit from the equa-

tion: $i = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ (A_1 and A_2 as prefactors), displaying the transfer rates of p-PTIC4Cl blends (τ_1 of 0.76 ps and τ_2 of 7.48 ps), and t-PTIC4Cl blends (τ_1 of 0.92 ps and τ_2 of 10.57 ps). It reveals that the p-PTIC4Cl blends possess faster hole transfer rates than that of t-PTIC4Cl blends. Together with the abovementioned device results, p-PTIC4Cl blends possess the better charge and exciton dynamics over the t-PTIC4Cl blends, hence improving the photovoltaic characteristics.

The surface morphologies of PBDB-TF:NFRAs blend films were investigated by atomic force microscopy (AFM), showing the TA treated PBDB-TF:p-PTIC4Cl blend film with the relatively smooth surface at the root-mean-square roughness of 0.98 nm (Fig. 4a and Fig. S6a in ESI). The blend films were also measured by GIWAXS (Fig. 4b and Fig. S6 in ESI). All the blend films possess the bi-model face-on and edge-on orientation relative to the substrate, as display from the coexistent (100) and (010) peaks in OOP and IP directions. The (010) peak at

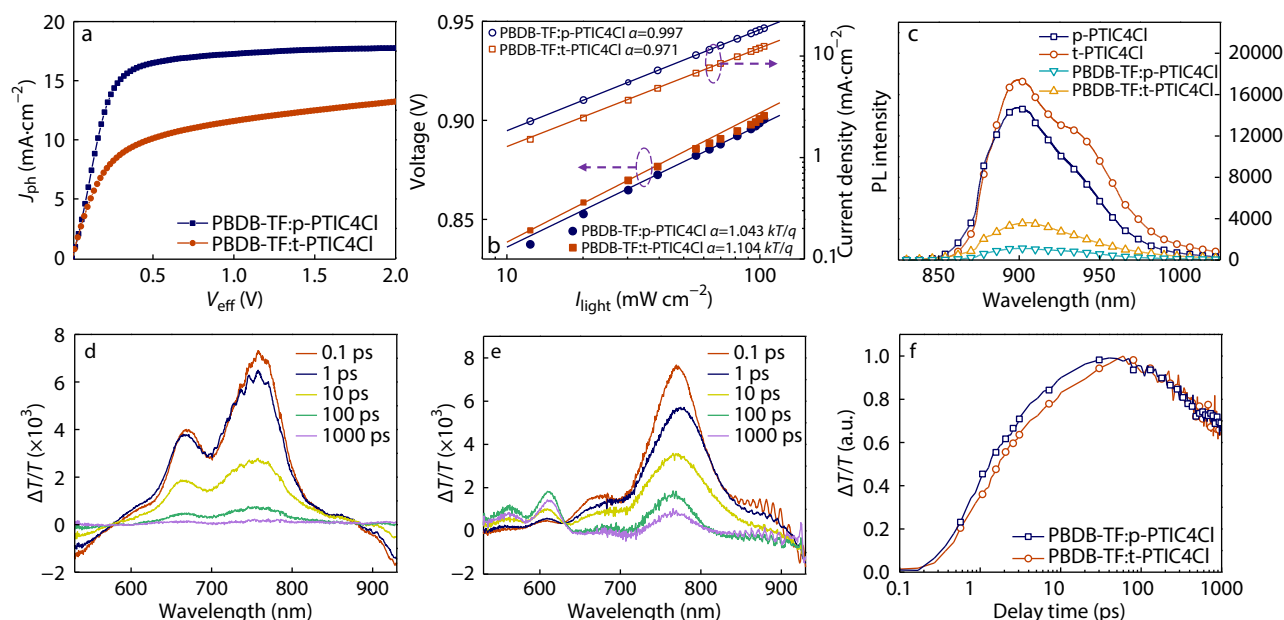


Fig. 3 (a) Photocurrent-effective voltage plots, and (b) dependencies of light intensities on the V_{oc} and J_{sc} of the PSCs; (c) PL of neat and blend films; Representative TA spectra of (d) p-PTIC4Cl film and (e) PBDB-TF:p-PTIC4Cl blend film at the indicated delay times, and (f) TA kinetics of hole transfer for PBDB-TF:NFRAs blend film.

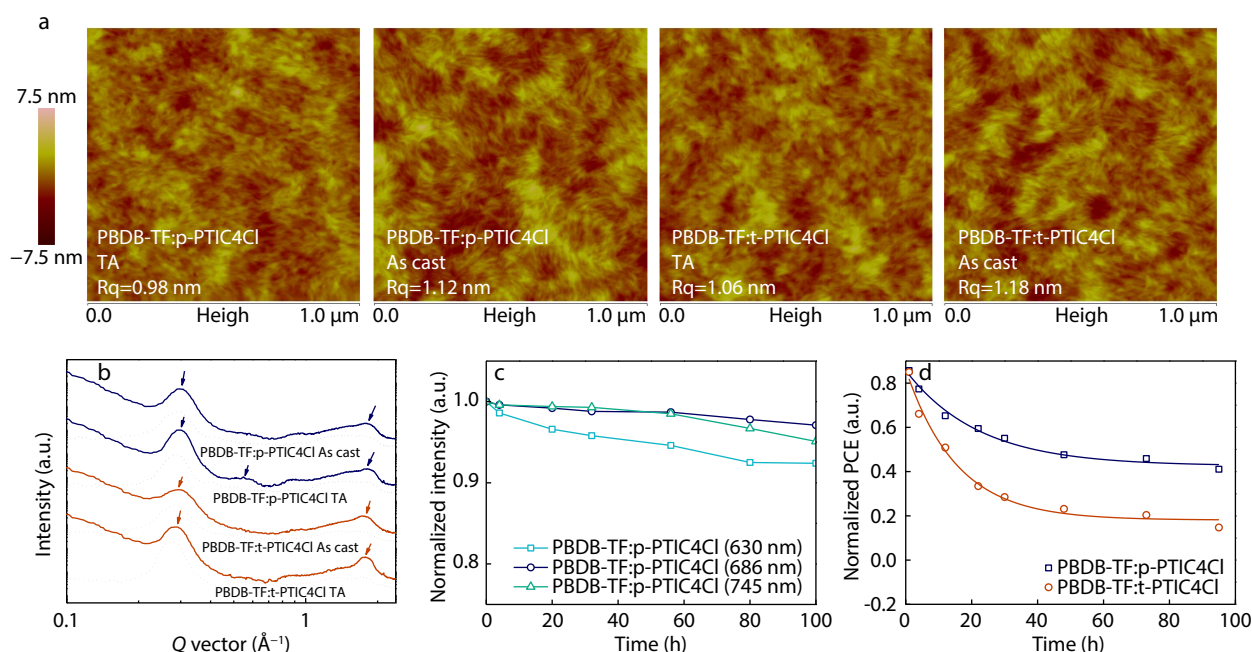


Fig. 4 (a) AFM height images and (b) GIWAXS profiles (solid line: out-of-plane, dashed line: in-plane) of PBDB-TF: NFRAs blend films in different conditions; (c) The change of absorption intensities for PBDB-TF:p-PTIC4Cl blend film under ultraviolet light of 365 nm in ambient; (d) Normalized PCE of PBDB-TF:NFRAs PSCs upon aging under AM 1.5G illumination ($100 \text{ mW} \cdot \text{cm}^{-2}$).

$q_z=1.8 \text{ \AA}^{-1}$ ($d=3.48 \text{ \AA}$) for PBDB-TF:p-PTIC4Cl and $q_z=1.74 \text{ \AA}^{-1}$ ($d=3.6 \text{ \AA}$) for PBDB-TF:t-PTIC4Cl corresponding to the π - π stacking of NFRA in blends (Fig. 1f). It reveals that the blend films with TA treatment display the enhanced peak intensities both in OOP and IP directions. Note the peak at $q_z=0.56 \text{ \AA}^{-1}$ ($d=11.22 \text{ \AA}$) in p-PTIC4Cl blend films in OOP direction is coincided with the long-range ordering feature observed from neat p-PTIC4Cl film. As for the TA treated t-PTIC4Cl blend film, the peak at $q_z=1.79 \text{ \AA}^{-1}$ ($d=3.51 \text{ \AA}$) became obviously sharper in OOP direction than that of as cast blend, implying the likely over aggregation of t-PTIC4Cl in the annealed blend films.

The photo stabilities of PBDB-TF:NFRAs blend films and PSCs are displayed in Figs. 4(c) and 4(d) and Fig. S7 (in ESI). It shows that PBDB-TF:p-PTIC4Cl blend film is quite stable with absorption peak intensities maintaining over 90% after 100 h ultraviolet light illumination (in ESI). Furthermore, under AM 1.5G illumination, PSCs exhibit the non-linear burn-in decay at the first 30 h, to 64% of initial PCEs for p-PTIC4Cl based devices and 38% of initial PCEs for t-PTIC4Cl based devices, and then subsequently transiting into the linear decay with steady photo stabilities to 100 hours. These results imply the simple NFRA and the derived PSCs have potentials to exhibit good photo stabilities under proper encapsulation.

CONCLUSIONS

In this work, we developed two fully non-fused ring acceptors, namely p-PTIC4Cl and t-PTIC4Cl, via a short synthetic route, wherein it has been revealed that the tuning of unaxisymmetric aromatic chains on thienyl bridge could modulate the self-assembly and stacking of these NFRA, hence impacting their optoelectronic and photovoltaic properties. Comparing with t-PTIC4Cl of 2-hexylthiophene chains, 3-hexylbenzene side chains, as six-member ring aromatic with large axis angle, possess a large torsion angle and high rotation barrier to the p-PTIC4Cl backbone. Upon pairing with PBDB-TF, the PCEs of PSCs have reached 11.30% for p-PTIC4Cl based devices, superior than 6.49% for t-PTIC4Cl based devices. Furthermore, the p-PTIC4Cl based blend films were also found to possess better exciton dissociation and charge transfer rates, as well as photo stability, to those of t-PTIC4Cl based blends. Overall, this work provides an effective strategy to optimize the optoelectronic properties of cost-effective electron acceptors.

NOTES

The authors declare no competing financial interest.



Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2750-0>.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 22125901), and National Key

Research and Development Program of China (No. 2019YFA0705900).

REFERENCES

- Chong, K.; Xu, X.; Meng, H.; Xue, J.; Yu, L.; Ma, W.; Peng, Q. Realizing 19.05% efficiency polymer solar cells by progressively improving charge extraction and suppressing charge recombination. *Adv. Mater.* **2022**, *34*, 2109516.
- Liu, Q.; Jiang, Y.; Jin, K.; Qin, J.; Xu, J.; Li, W.; Xiong, J.; Liu, J.; Xiao, Z.; Sun, K.; Yang, S.; Zhang, X.; Ding, L. 18% Efficiency organic solar cells. *Sci. Bull.* **2020**, *65*, 272–275.
- Song, J.; Zhu, L.; Li, C.; Xu, J.; Wu, H.; Zhang, X.; Zhang, Y.; Tang, Z.; Liu, F.; Sun, Y. High-efficiency organic solar cells with low voltage loss induced by solvent additive strategy. *Matter* **2021**, *4*, 2542–2552.
- He, C.; Bi, Z.; Chen, Z.; Guo, J.; Xia, X.; Lu, X.; Min, J.; Zhu, H.; Ma, W.; Zuo, L.; Chen, H. Compromising charge generation and recombination with asymmetric molecule for high-performance binary organic photovoltaics with over 18% certified efficiency. *Adv. Funct. Mater.* **2022**, *32*, 2112511.
- Wang, D.; Zhou, G.; Li, Y.; Yan, K.; Zhan, L.; Zhu, H.; Lu, X.; Chen, H.; Li, C. Z. High-performance organic solar cells from non-halogenated solvents. *Adv. Funct. Mater.* **2021**, *32*, 2107827.
- Tao, Y.; Liu, H.; Wang, D.; Zhao, F.; Chen, Z.; Zhu, H.; Chen, H.; Li, C. Z. Healing the degradable organic-inorganic heterointerface for highly efficient and stable organic solar cells. *InfoMat* **2022**, *4*, e12276.
- Hou, J.; Inganäs, O.; Friend, R. H.; Gao, F. Organic solar cells based on non-fullerene acceptors. *Nat. Mater.* **2018**, *17*, 119–128.
- Wei, Q.; Liu, W.; Leclerc, M.; Yuan, J.; Chen, H.; Zou, Y. A-DA'D-A non-fullerene acceptors for high-performance organic solar cells. *Sci. Chi. Chem.* **2020**, *63*, 1352–1366.
- Ren, J.; Shu, X.; Wang, Y.; Wang, D.; Wu, G.; Zhang, X.; Jin, Q.; Liu, J.; Wu, Z.; Xu, Z.; Li, C. Z.; Li, H. Key progresses of MOE key laboratory of macromolecular synthesis and functionalization in 2020. *Chin. Chem. Lett.* **2021**, DOI: 10.1016/j.ccl.2021.10.052.
- Yue, Q.; Liu, W.; Zhu, X. n-Type molecular photovoltaic materials: design strategies and device applications. *J. Am. Chem. Soc.* **2020**, *142*, 11613–11628.
- Wang, C.; Liu, F.; Chen, Q. M.; Xiao, C. Y.; Wu, Y. G.; Li, W. W. Benzothiadiazole-based conjugated polymers for organic solar cells. *Chinese J. Polym. Sci.* **2021**, *39*, 525–536.
- Chen, Z.; Ma, S. S.; Zhang, K.; Hu, Z. C.; Yin, Q. W.; Huang, F.; Cao, Y. A near-infrared non-fullerene acceptor with thienopyrrole-expanded benzo[1,2-b:4,5-b']dithiophene core for polymer solar cells. *Chinese J. Polym. Sci.* **2020**, *39*, 35–42.
- Zhang, Y.; Wang, Y.; Ma, R.; Luo, Z.; Liu, T.; Kang, S. H.; Yan, H.; Yuan, Z.; Yang, C.; Chen, Y. Wide band-gap two-dimension conjugated polymer donors with different amounts of chlorine substitution on alkoxyphenyl conjugated side chains for non-fullerene polymer solar cells. *Chinese J. Polym. Sci.* **2020**, *38*, 797–805.
- Liu, F.; Wang, D.; Li, J. Y.; Xiao, C. Y.; Wu, Y. G.; Li, W. W.; Fu, G. S. Side-chains engineering of conjugated polymers toward additive-free non-fullerene organic solar cells. *Chinese J. Polym. Sci.* **2020**, *39*, 43–50.
- Li, S.; Zhan, L.; Liu, F.; Ren, J.; Shi, M.; Li, C. Z.; Russell, T. P.; Chen, H. An unfused-core-based nonfullerene acceptor enables high-efficiency organic solar cells with excellent morphological stability at high temperatures. *Adv. Mater.* **2018**, *30*, 1705208.
- Zhang, Z. Q.; Zhang, S. H.; Liu, Z. X.; Zhang, Z. G.; Li, Y. F.; Li, C. Z.; Chen, H. Z. A simple electron acceptor with unfused backbone for polymer solar cells. *Acta Phys.-Chim. Sin.* **2019**, *35*, 394–400.
- Liu, Z. X.; Yu, Z. P.; Shen, Z.; He, C.; Lau, T. K.; Chen, Z.; Zhu, H.; Lu,

- X.; Xie, Z.; Chen, H.; Li, C. Z. Molecular insights of exceptionally photostable electron acceptors for organic photovoltaics. *Nat. Commun.* **2021**, *12*, 3049.
- 18 Yang, M.; Wei, W.; Zhou, X.; Wang, Z.; Duan, C. Non-fused ring acceptors for organic solar cells. *Energy Mater.* **2021**, *1*, 100008.
 - 19 Huang, H.; Guo, Q.; Feng, S.; Zhang, C.; Bi, Z.; Xue, W.; Yang, J.; Song, J.; Li, C.; Xu, X.; Tang, Z.; Ma, W.; Bo, Z. Noncovalently fused-ring electron acceptors with near-infrared absorption for high-performance organic solar cells. *Nat. Commun.* **2019**, *10*, 3038.
 - 20 Wu, Z.; Chen, Y.; Zhang, L.; Yuan, D.; Qiu, R.; Deng, S.; Liu, H.; Zhang, Z.; Chen, J. A ligand-free direct heteroarylation approach for benzodithiophenedione-based simple small molecular acceptors toward high efficiency polymer solar cells. *J. Mater. Chem. A* **2021**, *9*, 3314–3321.
 - 21 Geng, S. Z.; Yang, W. T.; Gao, J.; Li, S. X.; Shi, M. M.; Lau, T. K.; Lu, X. H.; Li, C. Z.; Chen, H. Z. Non-fullerene Acceptors with a thieno[3,4-c]pyrrole-4,6-dione (TPD) core for efficient organic solar cells. *Chinese J. Polym. Sci.* **2019**, *37*, 1005–1014.
 - 22 Wen, T. J.; Wang, D.; Tao, L.; Xiao, Y.; Tao, Y. D.; Li, Y.; Lu, X.; Fang, Y.; Li, C. Z.; Chen, H.; Yang, D. Simple near-infrared electron acceptors for efficient photovoltaics and sensitive photodetectors. *ACS Appl. Mater. Interfaces* **2020**, *12*, 39515–39523.
 - 23 Bi, P.; Zhang, S.; Ren, J.; Chen, Z.; Zheng, Z.; Cui, Y.; Wang, J.; Wang, S.; Zhang, T.; Li, J.; Xu, Y.; Qin, J.; An, C.; Ma, W.; Hao, X.; Hou, J. High-performance non-fused wide bandgap acceptor for versatile photovoltaic applications. *Adv. Mater.* **2022**, *34*, 2108090.
 - 24 Zhou, Y.; Li, M.; Lu, H.; Jin, H.; Wang, X.; Zhang, Y.; Shen, S.; Ma, Z.; Song, J.; Bo, Z. High-efficiency organic solar cells based on a low-cost fully non-fused electron acceptor. *Adv. Funct. Mater.* **2021**, *31*, 2101742.
 - 25 Chen, Y. N.; Li, M.; Wang, Y.; Wang, J.; Zhang, M.; Zhou, Y.; Yang, J.; Liu, Y.; Liu, F.; Tang, Z.; Bao, Q.; Bo, Z. A fully non-fused ring acceptor with planar backbone and near-IR absorption for high performance polymer solar cells. *Angew. Chem. Int. Ed.* **2020**, *59*, 22714–22720.
 - 26 Li, J.; Li, H.; Ma, L.; Xu, Y.; Cui, Y.; Wang, J.; Ren, J.; Zhu, J.; Zhang, S.; Hou, J. Influence of large steric hinderance substituent position on conformation and charge transfer process for non-fused ring acceptors. *Small Methods* **2022**, *6*, 2200007.
 - 27 Xue, Z. X.; Fang, J.; Li, J.; Zhang, D.; Xu, Z. W.; Liu, L. N.; Yao, J.; Ma, C. Q.; Li, W. S. Non-fused molecular photovoltaic acceptor with a planar core structure enabled by bulky and embracing-type side chains. *J. Mater. Chem. C* **2022**, *10*, 2945–2949.
 - 28 Lu, H.; Wang, X. D.; Wang, H.; Zhang, A. D.; Zheng, X. M.; Yu, N.; Tang, Z.; Xu, X. J.; Liu, Y. H.; Chen, Y. N.; Bo, Z. S. High-performance nonfused ring electron acceptor with a steric hindrance induced planar molecular backbone. *Sci. Chin. Chem.* **2022**, *65*, 594–601.
 - 29 Yu, Z. P.; Liu, Z. X.; Chen, F. X.; Qin, R.; Lau, T. K.; Yin, J. L.; Kong, X.; Lu, X.; Shi, M.; Li, C. Z.; Chen, H. Simple non-fused electron acceptors for efficient and stable organic solar cells. *Nat. Commun.* **2019**, *10*, 2152.
 - 30 Wen, T. J.; Liu, Z. X.; Chen, Z.; Zhou, J.; Shen, Z.; Xiao, Y.; Lu, X.; Xie, Z.; Zhu, H.; Li, C. Z.; Chen, H. Simple non-fused electron acceptors leading to efficient organic photovoltaics. *Angew. Chem. Int. Ed.* **2021**, *60*, 12964–12970.
 - 31 Wang, X.; Lu, H.; Liu, Y.; Zhang, A.; Yu, N.; Wang, H.; Li, S.; Zhou, Y.; Xu, X.; Tang, Z.; Bo, Z. Simple nonfused ring electron acceptors with 3D network packing structure boosting the efficiency of organic solar cells to 15.44%. *Adv. Energy Mater.* **2021**, *11*, 2102591.
 - 32 Ma, L.; Zhang, S.; Zhu, J.; Wang, J.; Ren, J.; Zhang, J.; Hou, J. Completely non-fused electron acceptor with 3D-interpenetrated crystalline structure enables efficient and stable organic solar cell. *Nat. Commun.* **2021**, *12*, 5093.
 - 33 Yang, Y.; Zhang, Z. G.; Bin, H.; Chen, S.; Gao, L.; Xue, L.; Yang, C.; Li, Y. Side-chain isomerization on an *n*-type organic semiconductor ITIC acceptor makes 11.77% high efficiency polymer solar cells. *J. Am. Chem. Soc.* **2016**, *138*, 15011–15018.
 - 34 Lin, Y.; Zhao, F.; He, Q.; Huo, L.; Wu, Y.; Parker, T. C.; Ma, W.; Sun, Y.; Wang, C.; Zhu, D.; Heeger, A. J.; Marder, S. R.; Zhan, X. High-performance electron acceptor with thienyl side chains for organic photovoltaics. *J. Am. Chem. Soc.* **2016**, *138*, 4955–61.
 - 35 Dou, K.; Wang, X.; Du, Z.; Jiang, H.; Li, F.; Sun, M.; Yang, R. Synergistic effect of side-chain and backbone engineering in thieno[2,3-f]benzofuran-based conjugated polymers for high performance non-fullerene organic solar cells. *J. Mater. Chem. A* **2019**, *7*, 958–964.
 - 36 Zhang, Z.; Liu, Z.-X.; Yan, K. R.; Li, H.; Liu, W.; Lu, X.; Li, H.; Chen, H.; Li, C. Z. Photovoltaic properties of DPP-based two-and three-component polymers. *Acta Polymerica Sinica* (in Chinese) **2018**, 295–303.
 - 37 Mai, J.; Xiao, Y.; Zhou, G.; Wang, J.; Zhu, J.; Zhao, N.; Zhan, X.; Lu, X. Hidden structure ordering along backbone of fused-ring electron acceptors enhanced by ternary bulk heterojunction. *Adv. Mater.* **2018**, *30*, 1802888.
 - 38 Xu, J.; Fu, W.; Yang, S.; Liu, T.; Li, C. Z.; Chen, H. Interface engineering in organic and organic/inorganic hybrid solar cells. *Acta Polymerica Sinica* (in Chinese) **2018**, 164–173.
 - 39 Zhou, G.; Zhang, M.; Chen, Z.; Zhang, J.; Zhan, L.; Li, S.; Zhu, L.; Wang, Z.; Zhu, X.; Chen, H.; Wang, L.; Liu, F.; Zhu, H. Marcus hole transfer governs charge generation and device operation in nonfullerene organic solar cells. *ACS Energy Lett.* **2021**, *6*, 2971–2981.
 - 40 Yu, Z. P.; Li, X.; He, C.; Wang, D.; Qin, R.; Zhou, G.; Liu, Z. X.; Andersen, T. R.; Zhu, H.; Chen, H.; Li, C. Z. High-efficiency organic solar cells with low voltage-loss of 0.46 V. *Chin. Chem. Lett.* **2020**, *31*, 1991–1996.